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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 **:**
C07C 25/00, 19/08, 2/02, C07F 15/00

A1

(11) International Publication Number: **WO 00/07968**

(43) International Publication Date: 17 February 2000 (17.02.00)

(21) International Application Number: PCT/US99/17519

(22) International Filing Date: 3 August 1999 (03.08.99)

(30) Priority Data:
09/127,796 3 August 1998 (03.08.98) US

(63) Related by Continuation (CON) or Continuation-in-Part (CIP) to Earlier Application
US 09/127,796 (CON)
Filed on 3 August 1998 (03.08.98)

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(81) Designated States: AU, CA, JP, NZ, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: COUPLING REACTIONS OF 2-SUBSTITUTED, 7-HALOINDENES WITH ARYL SUBSTITUENTS TO PRODUCE METALLOCENE CATALYST LIGANDS

(57) Abstract

Novel 2–substituted 7–haloindenes and methods for synthesizing such indenes are described. The 2–substituted 7–haloindenes may be coupled with any aryl group to produce a metallocene catalyst intermediate.

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COUPLING REACTIONS OF 2-SUBSTITUTED, 7-HALOINDENES WITH ARYL SUBSTITUENTS TO PRODUCE METALLOCENE CATALYST LIGANDS

This application is a continuation of Serial No. 09/127,796 filed 03 August 1998 and, in turn, a continuation-in-part of application Serial No. 08/795,019 filed 05 February 1997.

FIELD OF THE INVENTION

This invention relates to 2-substituted 7-haloindenes useful in coupling reactions to produce a wide variety of metallocene olefin polymerization catalyst intermediates and to metallocene catalysts derived from such intermediates.

BACKGROUND OF THE INVENTION

Metallocenes which comprise indene systems are well known α-olefin polymerization catalysts. Substitution patterns in such indene systems significantly influence poly-α-olefin properties, including tacticity and molecular weight.

Spaleck, et al., Organometallics (1994) 13:954-963 describes bridged zirconocene catalysts including indene systems illustrated by Compound 4 of "Scheme 1" (p. 955) which yield highly isotactic polypropylene when used with methylaluminoxane as a cocatalyst. As shown by

"Scheme 2", Compound 10, Spaleck's synthesis requires an expensive 2-(bromomethyl) biphenyl starting material.

This invention provides a more cost effective synthesis of metallocene catalysts which comprise indene systems.

DESCRIPTION OF THE FIGURES

Figure 1 illustrates a scheme for the synthesis of the Formula I compound, 2-methyl-7-chloroindene.

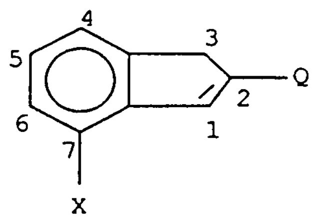
Figure 2 is a NMR spectrum of 2-methyl-7-chloroindene produced by the Figure 2 scheme as shown by Example 1.

Figure 3 illustrates a scheme for the synthesis of the Formula I compound, 2-ethyl-7-chloroindene.

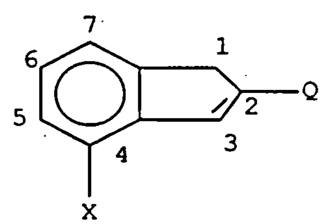
Figure 4 illustrates a scheme for Grignard reagent coupling a Formula I compound to provide a Formula II compound.

SUMMARY OF THE INVENTION

One aspect of this invention provides novel 2-substituted, 7-haloindenes of Formula I:

I. 

or I(a), i.e., the same compound to which different, but structurally identical ring position numbers are assigned:

I(a) 

Hereinafter the Formula I position numbers will be used.

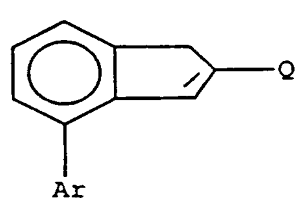
In Formula I and I(a), Q is a hydrocarbyl group and X is a halogen, i.e., fluorine, chlorine, bromine or iodine. Q may be an alkyl group R_1 which may be any straight or branched chain alkyl group having 1 to 10

carbon atoms. Q may also be any aryl group Ar. Specific Ar groups include phenyl, napthyl and anthracyl groups. Phenyl and substituted phenyl groups are preferred. Substitution may be at any one or more available ring positions by an alkyl group, e.g., R_1 or by an aryl group or any other substituent including a halogen.

Preferred embodiments of this aspect of the invention are substituted or unsubstituted 2-methyl-7-chloroindene and 2-phenyl-7-chloroindene.

Another aspect of the invention includes coupling of Formula I indenes with a Grignard reagent having the formula ArMgX to produce the novel compounds of Formula II:

II.



in which Q and Ar are as defined.

The invention accordingly comprises the novel Formula I and II compounds *per se*, procedures for the synthesis thereof, procedures for the conversion of Formula II compounds to intermediates for the production of metallocene catalysts and for the use of such catalysts to polymerize, e.g., an α-olefin.

DETAILED DESCRIPTION OF THE INVENTION

PREPARATION OF FORMULA I COMPOUNDS

Either of two methods, as shown by Examples 1 and 2 and Figures 1 and 3, may be used to prepare Formula I compounds.

THE EXAMPLE 1 METHOD

The starting material for the Example 1 method is a malonic acid diester having the Formula III:

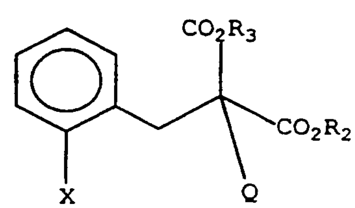
III. $$R_2OOC-\overset{\displaystyle Q}{\overset{|}{C}H}-COOR_3$$

in which Q (which is the same Q as in the Formula I and II compounds), R_2 and R_3 are the same or optionally different straight or branched chain alkyl groups having 1 to 10 carbon atoms. Alkyl groups specifically useful in this aspect of the invention include methyl,

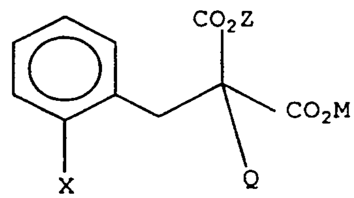
ethyl, propyl, isopropyl, butyl, isobutyl, pentyl, isopentyl, hexyl, isohexyl, heptyl, isoheptyl, octyl, isooctyl, nonyl, isononyl, decyl and isodecyl groups. Preferred diesters are methyl or phenyl diethyl malonate in which R is methyl and R_2 and R_3 are ethyl.

The malonic acid diester of Formula III is reacted with an alkali metal hydride MH, in which M is an alkali metal, i.e., lithium, sodium or potassium, to provide an intermediate compound in which the "H" of the Formula III diester is replaced by Z+, e.g., Na+. This reaction is appropriately carried out by adding a 40% to 60% dispersion of an alkali metal hydride in mineral oil to a non-interfering solvent such as tetrahydrofuran (THF) in a reaction vessel positioned in an ice bath. The malonic diester is added slowly while the temperature is maintained below 10°C. Hydrogen evolution is monitored. Upon completion of the addition of the diester, the reaction vessel is removed from the ice bath, and the reaction mixture containing the intermediate compound is stirred, e.g., for about 1 to 4 hours, preferably about 2 hours.

When the addition is complete, the reaction mixture containing the intermediate compound and which may contain THF is cooled to a temperature of 0°C to 10°C, preferably 5°C, and a 2-halobenzylhalide, preferably a 2-chloro or 2-bromobenzyl halide, is added over a time period of 0.5 to 1.5 hours to provide a reaction mixture containing a Formula IV compound. This reaction mixture is stirred, preferably at about ambient temperature, for 6 to 15, preferably about 12, hours:

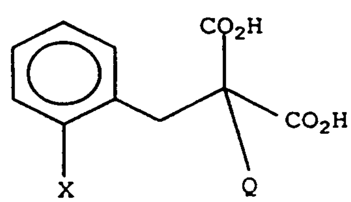
IV. 

in which X is the halogen substituent, preferably chlorine, of the Formula I compound. The Formula IV diester is saponified by heating, preferably in the presence of THF. The reaction mixture containing the diester is heated and combined with 30% to 60% aqueous alkali metal hydroxide MOH, preferably NaOH, to provide a compound having Formula V:

V. 

in which M is as defined.

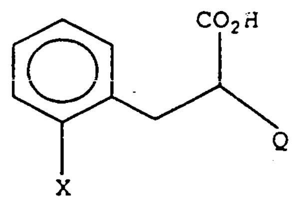
THF and the alcohols R_2OH and R_3OH, which result from saponification of the diester IV, are removed by distillation. The saponification reaction mixture is cooled, and poured into aqueous acid, e.g., 4-6N HCl, with vigorous stirring to produce a compound having Formula VI:

VI: 

The white solids comprising the Formula VI compound which form are removed by filtration, dried and placed in an appropriate reaction vessel equipped for short path distillation. Heating is applied to melt the solids and

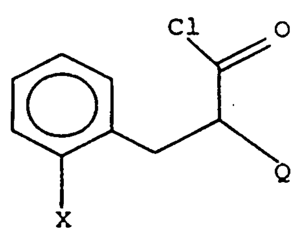
thereafter increased to 120°C to 150°C for a period of about 0.5 to 1.5 hours to accomplish decarboxylation and produce a compound of Formula VII:

VII.



The melt so produced is cooled to about 50°C, dissolved in a non-interfering solvent, e.g., an aliphatic hydrocarbon solvent having 6 to 9 carbon atoms, preferably heptane, and the Formula VII compound present in the solution is reacted with $SOCl_2$ at a temperature of 40 to 60°C with stirring to produce a Formula VIII compound:

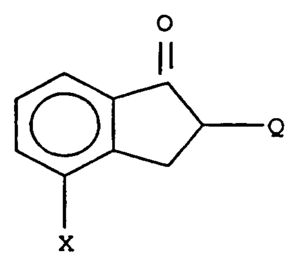
VIII.



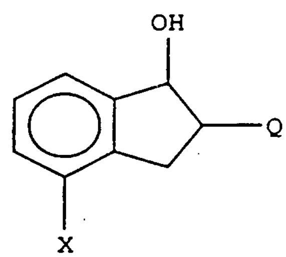
The temperature of the reaction mixture is thereafter raised to 100°C to 130°C to remove excess $SOCl_2$ and solvent. The reaction mixture is then cooled to room

temperature, a chlorinated hydrocarbon solvent, preferably methylene chloride, is added, and the mixture is cooled to -10°C to 0°C, followed by the addition of aluminum chloride with stirring to produce a compound of Formula IX by Friedel-Craft acylation:

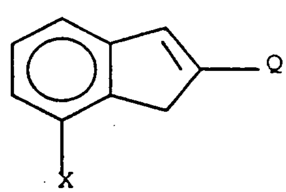
IX.



The acylation reaction is quenched by pouring on to ice. The layers which form are separated, and organic layer washed with an aqueous base, preferably sodium bicarbonate. All solvent is removed by distillation, methanol is added, and the reaction mixture containing Formula IX is cooled in an ice bath and combined with sodium borohydride to produce Formula X:

X. 

The reaction is quenched with water, and methylene chloride is added to separate the Formula X compound, and the solvent is removed by distillation. The Formula X compound is reacted with paratoluene sulfonic acid (pTSA) in toluene (or other aromatic solvent such as xylene or mesitylene) to afford the desired 2-substituted, 7-haloindene, compound of Formula XI:

XI. 

Aqueous and organic layers separate upon addition of aqueous sodium bicarbonate. The organic layer is dried over anhydrous Na_2SO_4. Toluene is removed by distillation.

EXAMPLE 1

Synthesis of 2-Methyl-7-Chloroindene. This example illustrates the scheme depicted by Figure 1.

A 5L round-bottom flask is equipped with a mechanical stirrer, thermometer and reflux condenser, and swept thoroughly with nitrogen. 2L tetrahydrofuran (THF) is added to the flask and then 116g NaH, 60% dispersion in mineral oil (2.9 mol). An ice bath is applied to the flask and moderate stirring begun. 506g methyl diethyl malonate (2.9 mol) is added slowly from an addition funnel maintaining the temperature below 10°C. Hydrogen evolution is monitored and vented through a mineral oil bubbler and controlled by the rate of addition of the methyl dimethyl malonate. Once the addition is complete, the cooling bath is removed, and the reaction stirred for 2 hours. The flask is again cooled to 5°C and 367 mL 2-chlorobenzylchloride (2.9 mol) added over 1 hour, then stirred for 12 hours at ambient temperature. Reflux condenser is changed to short path distillation. 520 mL 50% W/v NaOH(aq) and 1500 mL H_2O is added, then heating begun to distill the THF. Distillation was continued to 100°C with additional water to keep the reaction clear

and fluid. Distillation was continued to remove ethanol and water at 100°C for 15-30 minutes. Once cooled, the reaction mixture is poured into 1.5L H_2O and 1L 12N HCl with vigorous stirring. White solids, which formed immediately, were collected by filtration and dried on the Buchner funnel by aspiration for 15 minutes, then returned to the 5L flask equipped for short path distillation. Heating was applied slowly to melt the solids, and then increased to 135°C for at least 1 hour. CO_2 evolution was monitored by venting through a mineral oil bubbler. The melt was cooled to 50°C and 2L heptane added, then warmed to 45°C, and addition of 265 mL $SOCl_2$ (3.63 mol) was begun. Adequate venting was provided. After all the $SOCl_2$ was added, the reaction was stirred for 1.5 hours at 60°C, then heated to 120°C to distill the excess $SOCl_2$ and all the heptane. The reaction flask was allowed to cool to ambient temperature and 1.5L CH_2Cl_2 is added. Cooling was applied to -5° - 0°C, and 465g $AlCl_3$ (3.5 mol) added in portions. The reaction was stirred at ambient temperature for 2 hours, then quenched by pouring onto 2 Kg ice. The layers were separated, and the organic layer was washed with 500 mL H_2O, and then 250 mL 5% w/v

$NaHCO_3$(aq). All the solvent was distilled to a temperature of 70°C. 1L methanol was added to the oil, the flask cooled with an ice bath, and a slurry of 56g $NaBH_4$ (1.5 mol) in 500 mL methanol containing 1g $NaOCH_3$ was slowly added. Hydrogen evolution was monitored by venting through a mineral oil bubbler and controlled by the rate of addition. The reaction was quenched by adding 1.5L H_2O and 500 mL CH_2Cl_2 to separate the product. Solvent was distilled from the separated organic layer up to 70°C. 1.5L toluene was added to the oil and the 5L flask equipped with a Dean-Stark trap. Heating was begun and p-toluene sulfonic acid was added in 1-3g portions. The reaction was followed by GC until the dehydration was complete. 1.5L 5% w/v $NaHCO_3$(aq) was added to the reaction, the layers separated, and the organic layer dried over anhydrous Na_2SO_4. Toluene was distilled under reduced pressure to 90°C and the product, 2-methyl-7-chloroindene, obtained by distillation thorough a 30 cm packed column at 93-5°C at 1-3 mm Hg. Yield was 310g (1.89 mol), 65%, of a clear, colorless oil b.p. 229°C. Figure 2 was the NMR spectrum of the product.

EXAMPLE 1(a)

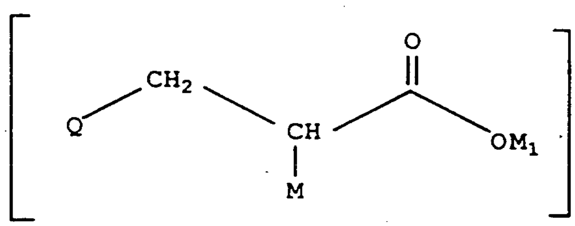
2-phenyl-7 chloroindene is prepared as described in Example 1 where phenyl diethyl malonate is used in lieu of methyl diethyl malonate.

THE EXAMPLE 2 METHOD

The starting material for the Example 2 method for producing Formula I compounds is an alkali metal, preferably sodium, salt, a carboxylic acid, preferably a fatty acid, e.g., butanoic acid, having the Formula QCOOM (XII) in which Q and M are as defined.

This Formula XII acid is reacted in THF solution with an alkali metal, preferably lithium, diisopropylamide, to form the intermediate XII:

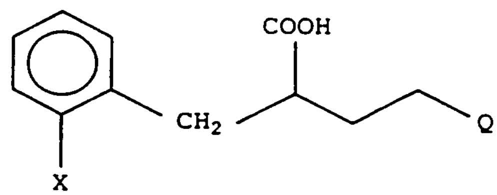
XII.



in which M and M_1 are alkali metals, and in which M is preferably lithium and M_1 is preferably sodium.

The Formula XII compound is reacted with a 2-halobenzylhalide to provide Formula XIII compound:

XIII.



in which X is a halogen, preferably chlorine or bromine, i.e., the halogen of a Formula I compound.

More specifically, this series of reactions may be carried out by combining an alkali salt of Formula XII with an alkali metal diisopropylamide, preferably lithium diisopropylamide to produce a compound having the Formula XII in THF solution. The reaction is conducted at ambient temperature and preferably stirred for 24 hours. 2-halo benzylhalide is added to the reaction mixture so produced, and the reaction mixture stirred for an additional time period, preferably 18 to 24 hours. The reaction is then quenched, e.g., by the addition of water. The aqueous layer is neutralized by a mineral acid, e.g., hydrochloric acid, at which point a phase separation occurs. A 2-

halobenzyl fatty acid, such as the compound of Formula XIII, is concentrated in the organic layer.

Synthesis of 2-Q-7-chloroindene is completed by the same sequence of reactions as described in Example 1 and shown in Figure 3, beginning with the addition of $SOCl_2$.

EXAMPLE 2

Synthesis of 2-Ethyl-7-Chloroindene. This example illustrates the scheme depicted by Figure 3.

A 12L round-bottom flask was equipped with a mechanical stirrer, thermometer and reflux condenser. 385g sodium butanoate (3.5 mol) and 2L THF were added to form a slurry. 2.625L lithium diisopropylamide, 2M in heptane/ THF/ethyl-benzene (5.25 mol, 50% excess) were added at ambient temperature, and then stirred for 24 hours. Then 705g 2-chlorobenzyl chloride (4.375 mol, 25% excess) was added, and the reaction stirred for another 24 hours. Once completed, the reaction was quenched by adding 1500 mL H_2O, and the solution allowed to separate. The aqueous layer, pH=13, was separated and neutralized by addition of 12N HCl to obtain pH=7.0, at which point a phase separation occurs. 2-(2-chlorobenzyl) butanoic acid was concentrated in the organic layer. Synthesis of 2-

ethyl-7-chloroindene was completed by the same sequence of reactions and method as described in Example 1, beginning with the addition of $SOCl_2$. See Figures 1 and 3. The product, 2-ethyl-7-chloroindene, was obtained by distillation at 110-114°C under 1-3 mm Hg. Yield was 205g (33% overall) of a clear, colorless oil.

PREPARATION OF FORMULA II COMPOUNDS

As shown by Figure 4, Formula II compounds are prepared in known manner by reacting a Formula I compound with a Grignard reagent, ArMgX, in which X is as described, preferably Br and Ar is as described, in an ethyl ether solvent containing 1-3-bis(diphenylphosphino) propane nickel II chloride, Ni(dpp).

Examples 3-6 utilize the synthesis of the Formula II compounds depicted by Figure 4.

EXAMPLE 3

A 5L round bottom flask was equipped with mechanical stirring, a reflux condenser and ice bath. 488.2g distilled 7-chloro-2-methylindene (2.97 mol) was added, dissolved in 2L ether and 32.2g Ni(dpp) (0.059 mol, 2 mol%) slurried in the solution, and stirred to cool to 0-2°C. 1.05L of 3.1M phenylmagnesium bromide in ether (3.25

mol, 10% excess) was added slowly from an addition funnel so that the temperature remained below 5°C. Once complete, the ice bath was removed, and the reaction stirred up to room temperature. The reaction was refluxed for 8 hours, and checked for completion by GC. The reaction flask was cooled with an ice bath, and 250 mL water added, then 1L 10% HCl. The aqueous and organic layers are separated, and the organic layer dried over anhydrous Na_2SO_4. Ether was distilled, and the residual oil placed on a column of 100g silica gel. Elution with hexane was performed, the hexane distilled under reduced pressure to a temperature of 90°C. 2-methyl-7-phenylindene (Spaleck compound 13a) was obtained by distillation at <1 mm Hg with a 36 cm Vigreux column at 125°C. A fore-cut containing biphenyl was obtained at 70-90°C and discarded. Yield was 507.8g (2.47 mol) equal to 80%.

EXAMPLE 3(a)

2-phenyl-7 phenyl indene is prepared in like manner from 2-phenyl 7 chloroindene as produced by Example 1(a).

EXAMPLE 4

A 12L flask equipped as in Example 3 was charged with 661g distilled 2-methyl-7-chloroindene (4 mol), 2.5L ether, and 43.3g Ni(dpp) (0.08 mol, 2 mol%). 1.75L of 2.6M phenylmagnesium bromide in ether (4.55 mol, 12% excess) was added at 2°C. Following stir-out to ambient temperature and reflux for 8 hours, the reaction was quenched and worked up by the method described in Example 3. Yield of 2-methyl-7-phenylindene (same as 2-methyl-4-phenylindene) was 642.7g (3.12 mol) equal to 78%.

EXAMPLE 5

A 5L flask was equipped as in Example 3. 178g 2-ethyl-7-chloroindene (1 mol), 1L ether and 10.8g Ni(dpp) (0.02 mol, 2 mol%) added, followed by 355 mL of 3.1M phenylmagnesium bromide in ether (1.1 mol, 10% excess). After quenching and work-up by the method described in Example 3, 176g 2-ethyl-7-phenylindene (0.8 mol) was obtained by vacuum distillation at 140°C in 80% yield.

EXAMPLE 5(a)

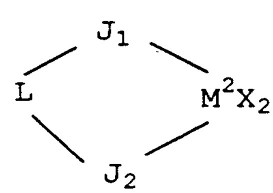
2-phenyl-7-napthylindene is prepared in like manner from 2-phenyl-7-chloroindene (see Example I(a)) and naphthyl magnesium bromide.

EXAMPLE 6

A 5L flask was equipped as described in Example 3. 164g 2-methyl-7-chloroindene (1 mol) 500 mL ether and 10.8g Ni(dpp) added. 2L of 0.5M naphthyl magnesium bromide in ether was added at 20°C. The reaction was stirred vigorously at reflux for 12 hours, then quenched and worked up as described in Example 3. 184.3g 2-methyl-7-(1-naphthyl)indene (Spaleck compound 21) (0.72 mol) was obtained by recrystallization from heptane in 72% yield.

METALLOCENE CATALYSTS

The Formula II compounds of this invention may be converted to metallocene α-olefin polymerization catalysts in the manner illustrated by Spaleck's Schemes 1 and 2 and in U.S. Patents 5,278,264 and 5,786,432. Such catalysts may have, for example, the formula



wherein J_1 and J_2 are the ligands from same or different Formula II compounds, L is $-SiY_2-$ in which Y is an alkyl group preferably having 1 to 5 carbon atoms or $-(CH_2)_n-$ in which n is 1 to 4 atoms, M^2 is Zr, Hf or Ti and X is a halogen, preferably chlorine. $-SiY_2-$ is preferably $-(CH_3)_2Si-$ and M_2X_2 is preferably $ZrCl_2$.

Example 7 illustrates one such conversion.

EXAMPLE 7

A 1L flask was charged with toluene (300 mL), THF (15g, 0.2 mol) and 2-methyl-7-naphthyl-indene (same as 2-methyl-4-napthyl indene) (52g, 0.2g). The contents were cooled to -20°C and 1.6 M butyl lithium in hexane (125 mL) was slowly added. This mixture was warmed to 25°C and stirred for four hours. The contents were cooled to -20°C and dimethyldichloro-silane (12.9g, 0.1 mol) was added. This reaction mixture was warmed to 25°C and stirred for twenty-four hours. Distill the reaction mixture under reduced pressure to pot temperature of 45°C. Allow the reaction to cool to ambient temperature and add ether (15g, 0.2 mol). The reaction mixture was then cooled to -20°C and 1.6 M butyl lithium in hexanes (125 mL, 0.2 mol) was

slowly added. This reaction mixture was slowly warmed to 25°C and stirred for twenty-four hours. Cool the reaction to -30°C and add zirconium tetrachloride, $ZrCl_4$ (23.2g, 0-1 mol). The reaction is allowed to warm to ambient temperature and stirring continued for another twelve hours.

The reaction mixture was then filtered and the solids were washed with hexane. The solids were dried under vacuum. The dry solids were dissolved in dichloromethane (800 mL) and this solution filtered through a small bed of celite to remove lithium chloride. The volume was reduced to 100 mL by solvent removal. The filtered crystals were washed with 10-15 mL dichloromethane and then dried in vacuum. The retained yield—60-80g 2 methyl-7-naphthyl-indene-$Si(CH_3)_2$ 7-napthyl-2-methyl indene.

EXAMPLE 7(a)

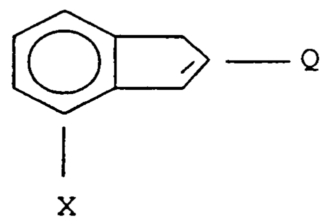
The 2-methyl-7-phenyl analog is produced in like manner from 2-methyl-7 phenylindene.

EXAMPLE 7(b)

In like manner 2-aryl-4-aryl ansa metallocenes may be prepared. Such metallocenes may include 2-phenyl-7-phenylindene $Si(CH_3)_2$-7-phenyl-2-phenylindene.

CLAIMS:

1. A compound having the formula:

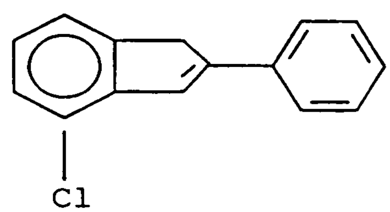


in which X is a halogen and Q is a hydrocarbyl group.

2. A claim 1 compound in which Q is an aryl group.

3. A claim 1 compound in which X is chlorine and Q is phenyl or napthyl.

4. A compound having the formula:



5. The method comprising reacting a compound having Formula I with ArMgX in which Ar is any aryl group and X is a halogen wherein a compound having Formula II is produced.

6. The claim 5 method in which Ar is a phenyl, a napthyl or a 9-fluorenyl group.

7. The claim 5 or claim 6 method in which X is chlorine or bromine or fluorine.

8. A method for synthesizing a compound having Formula I which comprises:

(i) reacting a malonic acid diester with an alkali metal hydride and a 2-halobenzylhalide to produce a compound having Formula IV;

(ii) saponifying said compound having Formula IV to produce a compound having Formula V;

(iii) converting said compound having Formula V to a compound having Formula VII;

(iv) reacting said compound having Formula VII with $SOCl_2$ to produce a compound having Formula VIII;

(v) reacting said compound having Formula VIII with aluminum chloride to produce a compound having Formula IX;

(vi) reacting said compound having Formula IX with sodium borohydride to produce a compound having Formula X; and

(vii) reacting said compound having the Formula X with paratoluene sulfuric acid to produce said compound having Formula I.

9. The claim 8 method in which:

(i) said malonic acid diester of step (i) has the Formula III; and

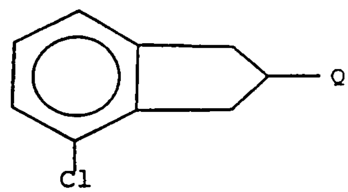
(ii) the alkali metal hydride of step (i) is sodium hydride, and the halobenzylhalide of step (i) is 2-chlorobenzyl chloride.

10. A method which comprises:

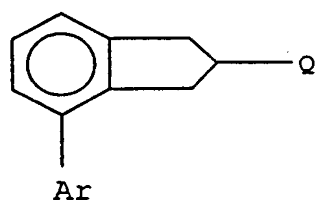
(i) reacting an alkali metal salt of a fatty acid having 1 to 10 carbon atoms with an alkali metal hydride to produce a first reaction mixture containing an intermediate compound; and

(ii) combining said step (i) reaction mixture with a 2-halobenzylhalide to convert said intermediate compound into a compound having the Formula XIV.

11. The method which comprises reacting a compound having the formula:



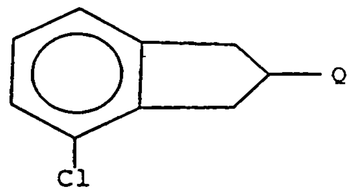
in which Q is a hydrocarbyl group with ArMgBr wherein a reaction mixture containing a compound having the Formula



is produced.

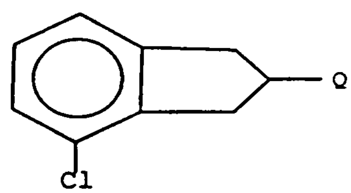
12. The claim 11 method in which ArMgBr is phenyl magnesium bromide or napthyl magnesium bromide.

13. The claim 11 method in which Q in the compound having the formula:



is phenyl or napthyl.

14. The claim 11 method in which Q in the compound having the formula:



is methyl and ArMgBr is phenyl MgBr.

15. A method which comprises reacting 7-chloro-2-phenylindene with naphthyl magnesium bromide, wherein a reaction mixture containing 7-naphthyl 2-phenylindene is produced.

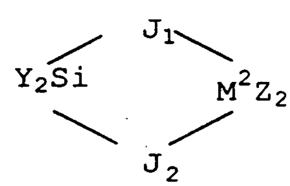
16. The claim 15 method in which said 7-naphthyl-2-phenylindene is separated from said reaction mixture.

17. A method which comprises

(i) reacting a compound having Formula I with ArMgX in which Ar is phenyl, napthyl or anthracyl groups and X is a halogen

wherein a compound having Formula II is produced; and

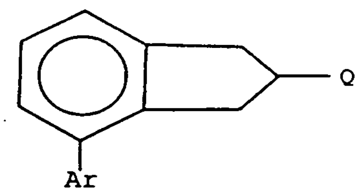
(ii) converting said compound of Formula II produced in step (i) to a compound having the formula



wherein J_1 and J_2 are the same or different Formula II compound residues, Y is an alkyl group, M^2 is a group IV metal and Z is chlorine, bromine, fluorine or iodine.

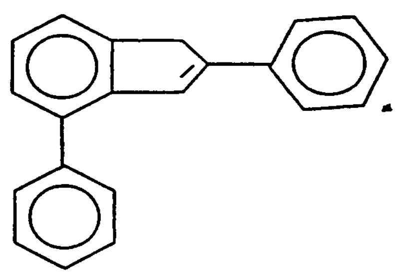
18. The claim 17 method wherein Y is methyl and Z is chlorine.

19. A compound having the formula:



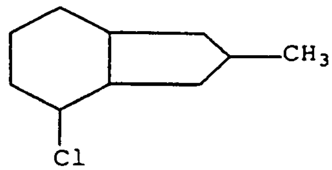
in which Q is a hydrocarbyl group and Ar is an aryl group.

20. A compound having the formula:

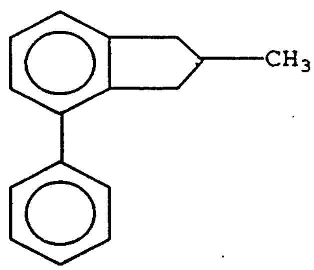


21. A method which comprises:

(i) reacting a compound having the formula (a):

(a) 

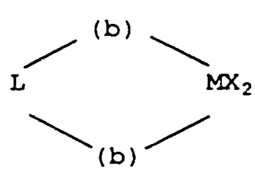
with phenyl magnesium bromide wherein a reaction mixture containing a compound having the formula (b)

(b) 

is produced.

22. The claim 21 method further comprising a step (ii):

(ii) converting said step (i) compound of formula (b) to a metallocene of formula (c):

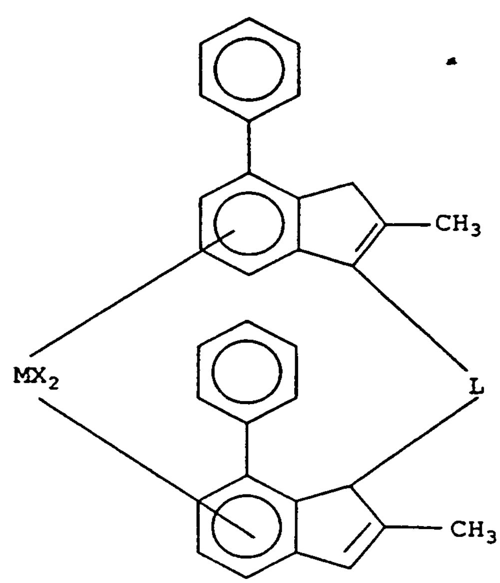
(c) 

wherein L is $-Si(Y_2)-$ in which Y is an alkyl group or $(CH_2)_n$ in which n is 1 to 4, M is Zr, Hf or Ti and X is a halogen.

23. A method for producing 2-methyl-4-phenylindene which comprises

(i) reacting 2-methyl-4-chloroindene with phenyl Grignard reagent wherein a reaction mixture containing 2-methyl-4-phenylindene is produced; and

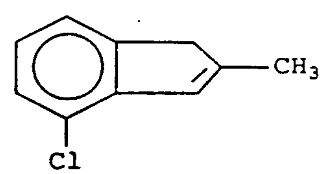
(ii) converting said 2-methyl-4-phenylindene of step (i) to a metallocene having the formula



in which L is $-Si(Y)_2$ in which Y is an alkyl group having 1 to 5 carbon atoms, M is Zr, Hf, or Ti and X is a halogen.

24. A method for synthesizing 2-methyl-4-phenylindene which comprises:

(i) reacting a compound having



with phenyl magnesium bromide wherein a reaction mixture containing said 2-methyl-4-phenylindene is produced.

25. The claim 24 method further comprising:

(ii) converting said 2 methyl-4-phenylindene from step (i) into bis(2-methyl-4-phenyl)zirconium.

26. The claim 24 method further comprising converting said 2-methyl-4-phenylindene from step (i) into rac-dimethylsilylbis (2-methyl-4-phenyl indenyl) zirconium dichloride.

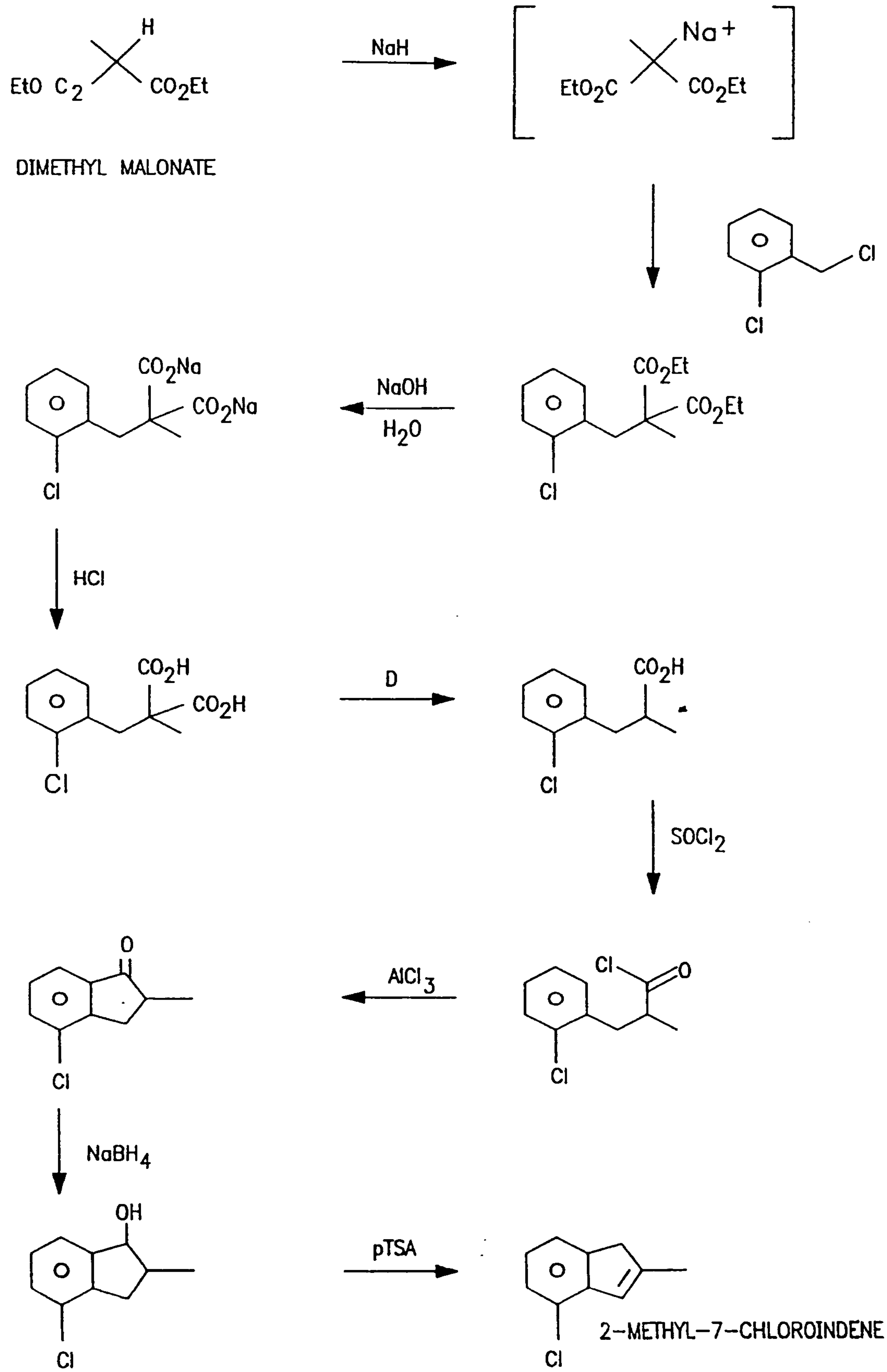

H
EtO C 2
CO2Et
DIMETHYL MALONATE
NaH
Na+
EtO2C
CO2Et
Cl
Cl
CO2Na
CO2Na
Cl
NaOH
H2O
CO2Et
CO2Et
Cl
HCl
CO2H
CO2H
Cl
D
CO2H
Cl
SOCl2
O
Cl
AlCl3
Cl
O
Cl
NaBH4
OH
Cl
pTSA
Cl
2-METHYL-7-CHLOROINDENE

FIG. 1

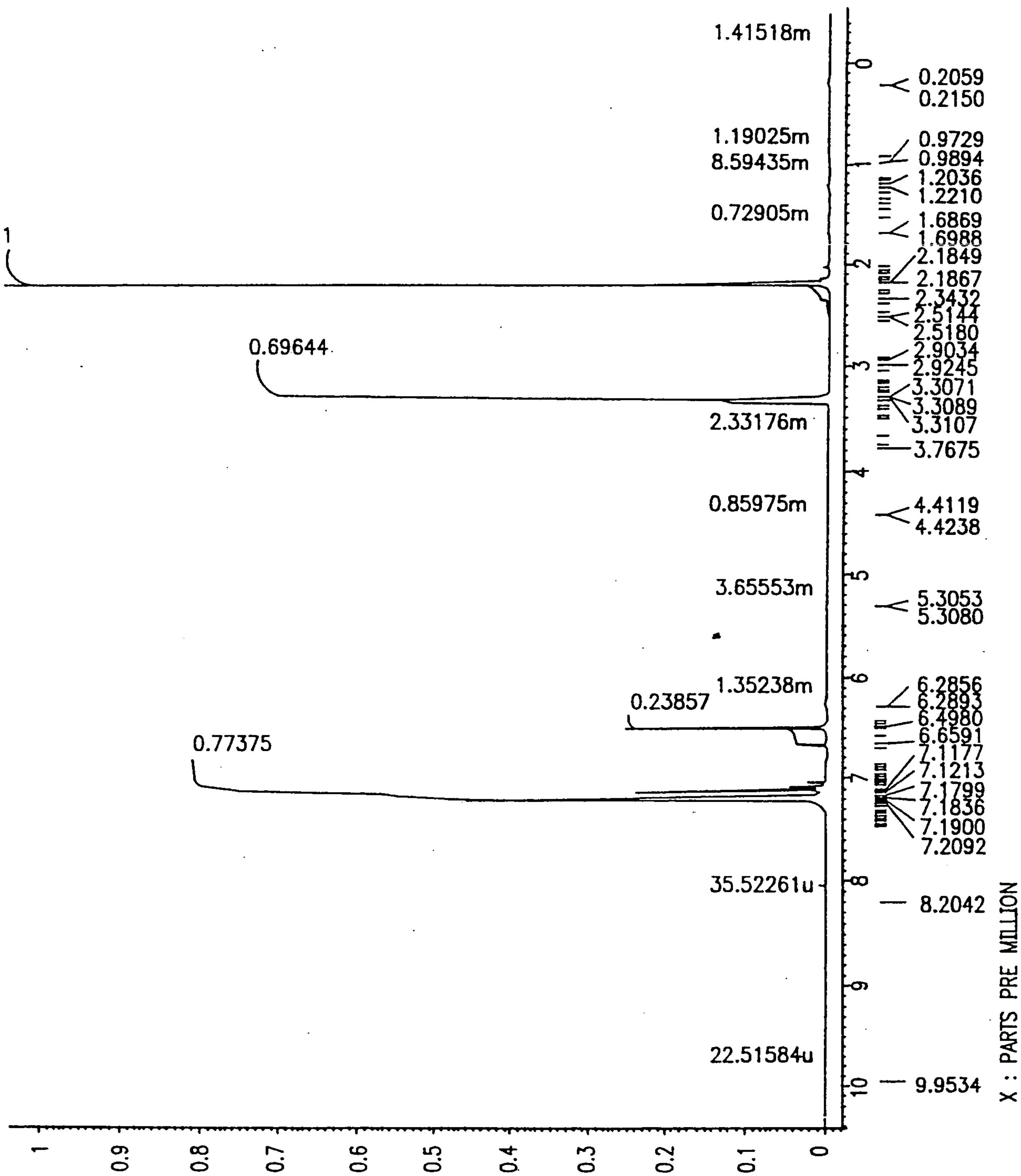
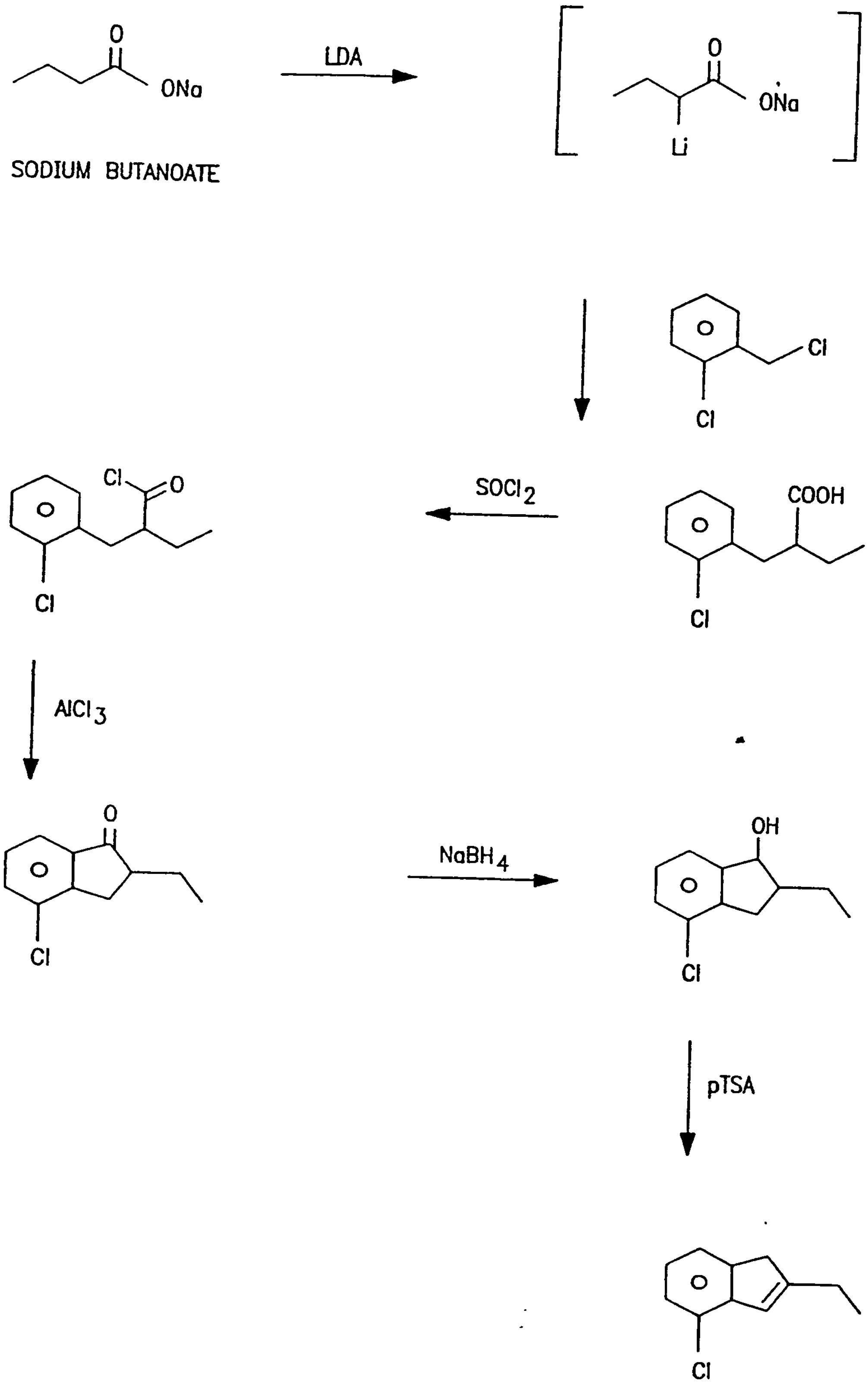
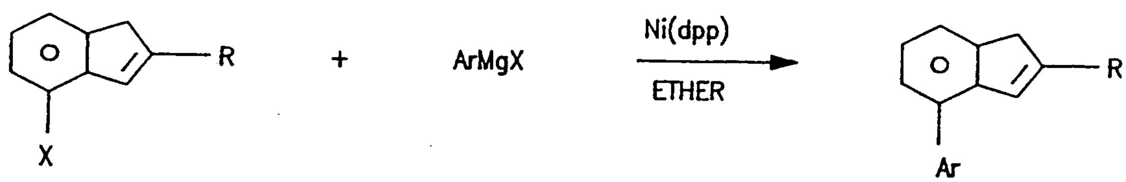

1.41518m
1.19025m
8.59435m
0.72905m
1
0.69644
2.33176m
0.85975m
3.65553m
1.35238m
0.23857
0.77375
35.52261u
22.51584u
0.2059
0.2150
0.9729
0.9894
1.2036
1.2210
1.6869
1.6988
2.1849
2.1867
2.3432
2.5144
2.5180
2.9034
2.9245
3.3071
3.3089
3.3107
3.7675
4.4119
4.4238
5.3053
5.3080
6.2856
6.2893
6.4980
6.6591
7.1177
7.1213
7.1799
7.1836
7.1900
7.2092
8.2042
9.9534
X : PARTS PRE MILLION

FIG. 2



2-ETHYL-7-CHLOROINDENE

FIG. 3



[I]

[II]

X= Cl,Br,I

Ar=aryl

R=alkyl or aryl

FIG. 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/17519

A. CLASSIFICATION OF SUBJECT MATTER
IPC(6) :C07C 25/00, 19/08, 2/02; C07F 15/00
US CL :570/127, 129, 183; 585/427; 556/11
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 570/127, 129, 183; 585/427; 556/11

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2,953,609 A (WADSWORTH ET AL) 20 September 1960, see entire document.	1-4
A	US 4,219,687 A (DOLHYJ ET AL) 26 August 1980, see entire document.	11-16, 19-21, 23, 24
A	US 5,602,228 A (WANG ET AL) 11 February 1997, see entire document.	11-16, 19-21, 23, 24
A, E	US 5,965,759 A (LIN) 12 October 1999, see entire document.	22, 25, 26
A, E	US 5,936,108 A (LIN ET AL) 10 August 1999, see entire document.	22, 25, 26

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 15 OCTOBER 1999	Date of mailing of the international search report 04 NOV 1999
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer ALAN SIEGEL Telephone No. (703) 308-0196

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/17519

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 5-10, 17 and 18
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

Reference is made to formulas which are not defined in the claims.

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.